

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q83325

Yoshiyuki OGUCHI, et al.

Appln. No.: 10/508,859

Group Art Unit: 2871

Confirmation No.: 8700

Examiner: Nathanael R. Briggs

Filed: December 21, 2004

For: METHOD FOR MANUFACTURING LIQUID CRYSTAL DISPLAY DEVICE,
SUBSTRATE FOR LIQUID CRYSTAL DISPLAY DEVICE, METHOD FOR
MANUFACTURING SUBSTRATE FOR LIQUID CRYSTAL DISPLAY DEVICE, AND
SPACER PARTICLE DISPERSION

DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Mr. Michihisa Ueda, hereby declare and state the following.

I am a citizen of Japan.

I have received the degree of Master of Chemical Science, Faculty of Science, Osaka
City University, Osaka.

I have been employed by SEKISUI CHEMICAL CO., LTD from 1989 to the present,
where I hold a position as a researcher in chemical technologies.

I am a named inventor in the present U.S. Application No. 10/508,859.

The following Experiment was performed by me or under my supervision. The
Experiment illustrates the effect of the content of vinyl-based monomers on dispersibility,

location of spacer particles, display quality of a liquid crystal display cell, and the purity of a liquid crystal of the dispersion of spacer particles.

Experimental Procedures

A. Preparation of spacer dispersion

(Experimental Example 1)

(1) Preparation of spacer seed particles

To a separable flask 15 parts by weight of divinylbenzene, 5 parts by weight of isooctyl acrylate and 1.3 parts by weight of benzoyl peroxide as an initiator were charged and mixed uniformly. Next, to this mixture 20 parts by weight of a 3% by weight aqueous solution of polyvinyl alcohol (trademark "KURARAY Poval GL-03" made by KURARAY CO., LTD.) and 0.5 parts by weight of sodium dodecyl sulfate were charged and stirred uniformly, and then 140 parts by weight of ion-exchanged water was added. Then, this aqueous solution was polymerized at 80°C for 15 hours under nitrogen flow while being stirred to obtain fine particles. The obtained fine particles were adequately washed with hot water and acetone, and then classified and the acetone was volatilized to obtain spacer seed particles. An average particle diameter of the obtained spacer seed particles was 5 μm and a CV value was 3.0%.

(2) Preparation of spacer particles

5 parts by weight of the obtained spacer seed particles was charged to mixed monomers comprising 20 parts by weight of dimethyl sulfoxide, 2 parts by weight of hydroxyethyl

methacrylate, 12 parts by weight of i-butyl methacrylate, 4 parts by weight of methyl methacrylate, and 2 parts by weight of methacrylic acid and dispersed with a sonicator, and then the mixture was stirred uniformly. Next, a reaction system was replaced with a nitrogen gas and the mixture was stirred at 30°C for 2 hours. Then, to the reaction system was added 10 parts by weight of a 0.1 mol/liter aqueous solution of diammonium cerium nitrate ($[\text{Ce}(\text{NH}_4)_2](\text{NO}_3)_6$) regulated by a 1N aqueous solution of nitric acid, and after a polymerization reaction was conducted for 5 hours, a reactant was taken out and separated into particles and a reaction solution through filtration using a 3 μm membrane filter. The obtained particles were adequately washed with ethanol and acetone and then dried under reduced pressure with a vacuum drier to obtain spacer particles, in which a vinyl-based thermoplastic resin is formed on the surface of the spacer seed particle by graft polymerization.

(3) Preparation of medium

60 parts by weight of ethylene glycol, 20 parts by weight of isopropyl alcohol and 20 parts by weight of ion-exchanged water were uniformly mixed and stirred to prepare a medium.

(4) Preparation of spacer dispersion

0.5 parts by weight of the spacer particles was gradually added to 100 parts by weight of medium, and uniformly mixed and stirred with a sonicator to prepare a dispersion of spacer.

(Experimental Examples 2 to 7)

By following the same procedure as in Experimental Example 1 except for changing the composition of the mixed monomers as shown in Table 1, spacers in which a vinyl-based thermoplastic resin is formed on the surface of the spacer seed particle by graft polymerization were prepared, in addition to spacer dispersions.

Table 1

		Experimental Example						
		1	2	3	4	5	6	7
Spacer seed particles (part by weight)		5	5	5	5	5	5	5
Composition of mixed monomers (part by weight)	Isobutyl methacrylate	12	4	14	12	8	4	2
	Methyl methacrylate	4	10	—	—	—	—	—
	Hydroxyethyl methacrylate	2	4	6	6	10	14	18
	Methacrylic acid	2	2	—	2	2	2	—
	Dimethyl sulfoxide	20	20	20	20	20	20	20

B. Evaluation

The dispersibility of the dispersions of spacer particles prepared in Experimental Example 1 to 7, the property of locating spacer particle when the dispersion of spacer particles is ejected onto the substrate, the display quality as a liquid crystal display, and the purity of liquid crystal were evaluated as described below.

The results of the evaluation are shown in Table 2, below.

(Evaluation of the dispersibility of dispersion of spacer particles)

The clogging in filtering the dispersion of spacer particles with a stainless screen having a mesh size of 10 μm and the re-dispersion of the precipitated spacer particles were visually observed and the dispersibility was evaluated according to the following criteria:

⊙: There was little clogging on the stainless screen and the dispersion of spacer particles passed through it smoothly. Further, the re-dispersion of the spacer particles was good.

○: The dispersion of spacer particles passed through the stainless screen, but some clogging was found on the stainless screen after filtration. Further, the re-dispersion of the spacer particles was good.

△: There was much clogging on the stainless screen and the dispersion of spacer particles did not pass through the screen smoothly. The dispersion of spacer particles could be filtered, but it took a great deal of time. The precipitated spacers could not be re-dispersed, even if the container were shaken.

×: Clogging on the stainless screen was serious and the dispersion of spacer particles did not pass through the screen at all. The precipitated spacers could not be re-dispersed, even if the container were shaken.

(Evaluation of the property of locating spacer particles)

The dispersion of spacer particles was filtered with a stainless screen (mesh size of 10 μm) to remove cohesion spacers and then ejected onto a substrate using an ink-jet system of a piezo ink-jet method, on which a head having a nozzle hole diameter of 30 μm was mounted.

As the substrate, there was used a substance provided with an orientation layer formed by applying uniformly a polyimide intermediate ("LP-64" made by Toray Industries, Inc.) to a color filter glass substrate, on the surface of which a ITO transparent electrode was provided, using spin coater, drying at 150°C and then baking at 280°C for 90 minutes to cure. Since a black matrix of 20 μm in width is formed between pixels of a color filter on the above color filter substrate, it was selected to locate spacer at 150 μm spacing on this black matrix with an ink-jet system. And, the spacer was adjusted and located in such a way that a distribution density of the spacers was 100 particles/ mm^2 . During the ejection of the above spacer, a substrate of room temperature was placed on a stage and the substrate, to which ejection of spacers was completed, was immediately shifted to on a hot plate heated to 90°C and dried.

After visually recognizing that the medium was completely dried, the substrate was allowed to stand at the as-is temperature for 30 minutes. After the spacer particles were located on the substrate by the above-mentioned method, a status of the spacer particles located was observed by a microscope and a property of locating spacer particle was evaluated according to the following criteria.

◎: Each line which the spacer particles are located has an equal distance between lines and is straight, and no light leakage was found.

○: Each line which the spacer particles are located has an equal distance between lines and is straight, but a little light leakage was found.

△: Each line which the spacer particles are located has a different distance between lines and much light leakage was found.

×: Since the spacer particles were little ejected onto the substrate, they were not located and much light leakage was found.

(Evaluation of display quality of liquid crystal display)

In order to bond a substrate (color filter substrate) in which the spacer particles were located as described above to an opposed array substrate, a peripheral sealing material was printed by a screen printing method, and both substrates were bonded with this sealing material and then the sealing material was cured by heating at 160°C for 90 minutes to produce an empty cell with a cell gap of 5 μm . Then, a predetermined amount of liquid crystal was filled into the empty cell by a vacuum method, and after a filling port was sealed with an end-sealing material, the end-sealing material was treated by heat at 120°C for 30 minutes to manufacture a liquid crystal display.

The evaluation proceeded according to the following criteria by visually observing the images magnified by an electron microscope after a voltage of 4.2 V applied five times.

○: In a display area, a very few little light leakages were found and display quality of liquid crystal display was excellent.

△: little light leakages were found around a spacer particle that was overrun into a display area.

×: In a display area, little light leakages were clearly found around a spacer particle that was overrun into a display area. Further, the display quality of the liquid crystal display was wrong.

(Evaluation of the purity of the liquid crystal)

0.1 g of spacer particles was dispersed in 2 ml of liquid crystal (trade name “ZLI-4720-000”, made by Merck Ltd.) and a dispersion was allowed to stand at 80°C for 200 hours, and then liquid crystal was recovered and the purity of the liquid crystal was measured by gas chromatography.

Results

Table 2

			Experimental Example						
			1	2	3	4	5	6	7
dispersion of spacer particles	the content of the vinyl-based monomer (% by weight)	a vinyl-based monomer having a hydrophilic functional group	20	30	30	40	60	80	90
		a vinyl-based monomer having an alkyl group	60	20	70	60	40	20	10
		other monomers	20	50	—	—	—	—	—
	Surface tension at 20°C of Medium (mN/m)		35	35	35	35	35	35	35
Evaluation	Dispersibility		△	○	△	○	◎	◎	◎
	Property of location spacer particles		○	○	○	○	◎	◎	◎
	Display quality of liquid crystal display cell		◎	◎	◎	◎	◎	◎	△
	Purity of liquid crystal (%)		100	100	100	100	100	100	100

Table 2 above shows that when the mixture of vinyl-based monomers contains a vinyl-based monomer having a hydrophilic functional group in an amount of 30 to 80% by weight and a vinyl-based monomer having an alkyl group having 3 to 22 carbon atoms in an amount of 20 to 60% by weight (see Experimental Examples 2, 4, 5, and 6), the “dispersibility,” the “property of location spacer particles,” the “display quality of liquid crystal display cell,” and the “purity of the liquid crystal” properties are all excellent.

U.S. Application No.: 10/508,859

Conversely, Table 2 also shows that when the content of the vinyl-based monomer having the above hydrophilic functional group in the vinyl-based monomer is 20% by weight (Experimental Example 1), it becomes difficult to disperse the spacer particle in the medium. In addition, when the content of the vinyl-based monomer having the above hydrophilic functional group in the vinyl-based monomer is 90% by weight (Experimental Example 7), the display quality of the liquid crystal display cell worsened. Experimental Example 3 further shows that when the content of the vinyl-based monomer having the above alkyl group having 3 to 22 carbon atoms in the vinyl-based monomer is 70% by weight, the "dispersibility" worsened, as well.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 9. 25. 2008

Michihisa Ueda
Michihisa Ueda